Letter to the Editor

RAMAN SPECTRA OF SOLUTIONS OF O-DICHLORO-BENZENE IN METHYLCYCLOHEXANE

D. C. BISWAS

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA 32.

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It was observed recently (Biswas, 1955) in an investigation on the Raman spectra of dichlorobenzenes in different states and at different temperatures that two intense lines appear at 469 cm^{-1} and 487 cm^{-1} in the Raman spectrum of *o*-dichlorobenzene in the liquid phase and when the liquid is solidified the two lines are replaced by an intense single line at 478 cm^{-1}. It was suggested that the line 469 cm^{-1} might be due to dimers present in the liquid and the corresponding line due to the single molecule was at 487 cm^{-1}. As solvent molecules have much influence on molecular association in such a case it might be expected that if the substance would be dissolved in suitable solvents the relative intensities of the two lines due to the monomer and the dimer respectively would change appreciably. Recently, methylcyclohexane has been found to be a very good solvent for this purpose (Sirkar and Kastha, 1955) and therefore, the Raman spectra of solutions of *o*-$C_6H_4Cl_2$ in methylcyclohexane have been investigated to test the above hypothesis.

A comparison of spectrograms due to the pure liquid and the solutions of this substance in methylcyclohexane reproduced in figure 1 shows that the

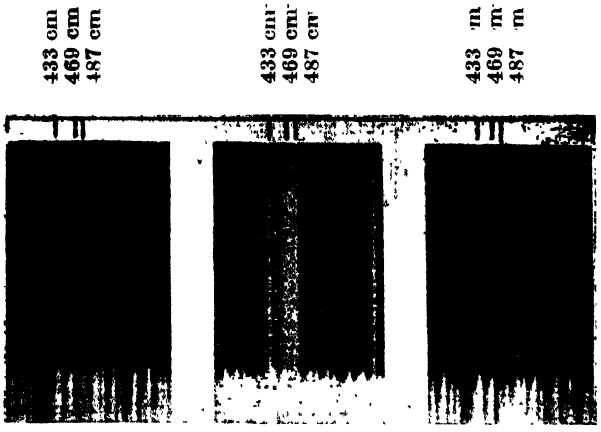

Fig. 1

solvent has great influence on the relative intensities of the two lines mentioned above. The integrated intensities of the two lines at 469 cm^{-1} and 487 cm^{-1} are

nearly the same in the Raman spectrum due to the pure liquid at room temperature. The spectrogram due to a 40% solution of this substance in methylcyclohexane shows that the intensity of the line 469 cm^{-1} is less than half that of the line at 487 cm^{-1}. When the strength is reduced to 20% by volume, the line 469 cm^{-1} becomes broader and appears as a very weak and diffuse satellite of the intense line at 487 cm^{-1}. Again, on comparing the intensities of both these lines with the line at 433 cm^{-1} it can be seen clearly that the line 469 cm^{-1} becomes much weaker and the line 487 cm^{-1} becomes relatively much stronger when *o*-$C_6H_4Cl_2$ is dissolved in methylcyclohexane. It is thus evident that in dilute solutions of methylcyclohexane the Raman line at 487 cm^{-1} becomes stronger at the expense of the other line at 469 cm^{-1}.

The above results furnish conclusive evidence in support of the suggestion (Biswas, 1955) that the line 469 cm^{-1} of the liquid *o*-$C_6H_4Cl_2$ is due to a dimer and the line 487 cm^{-1} is due to the same mode in the single molecule. The line 487 cm^{-1} was attributed to the vibration of the benzene ring of mode ϵ_g^+ (Nordheim and Sponer, 1943). In the liquid state this vibration is influenced by the field of the neighbouring polar molecules of the substance and a second line corresponding to the same mode in a dimer formed in the liquid state is produced at 469 cm^{-1}. The relative intensities of these two lines suggest that in the liquid state at room temperature nearly 50% of the molecules are in the associated state. When the strength of this solution is only 15% by volume, the number of associated molecules becomes negligibly small and the intensity of the line at 469 cm^{-1} due to the dimer is reduced to a very low value.

One of the three lines in the neighbourhood of 200 cm^{-1} observed in the spectra due to *m*-dichlorobenzene, *m*-chlorotoluene and *m*-bromotoluene was attributed to dimers (Biswas, 1955). This line, however is found to persist even in the case of very dilute solutions of these substances in methylcyclohexane. An alternative assignment is, therefore, to be found as the line seems to be due to the single molecule.

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REFERENCES

Biswas, D. C., 1955a, *Ind. J. Phys.*, **29**, 179.

Biswas, D. C. 1955b, *Ind. J. Phys.*, **29**, 257.

Nordheim, G., and Sponer, H., 1943, *J. Chem. Phys.*, **11**, 253.

Sirkar, S. C., and Kastha, G. S., 1955, *J. Chem. Phys.*, **23**, in press.